

[54] **ION EXCHANGE STRENGTHENED GLASS CONTAINING P₂O₅**

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 605,108, Aug. 15, 1975, Pat. No. 4,015,045, which is a continuation-in-part of Ser. No. 432,006, Jan. 9, 1974, abandoned.

[51] **Int. Cl.² B32B 17/00; C03C 21/00**

[52] **U.S. Cl. 428/410; 106/52; 65/30 E; 65/30 R; 428/218**

[58] **Field of Search 428/410, 218; 65/30 R, 65/30 E; 106/52**

[56] **References Cited**

U.S. PATENT DOCUMENTS

3,357,876	12/1967	Rinehart	65/30 E
3,485,647	12/1969	Harrington	65/30 E
3,485,702	12/1969	Mochel	65/30 E
3,498,773	3/1970	Grubb	65/30 E
3,498,801	3/1970	Keul	106/39.7
3,778,335	12/1973	Boyd	65/30 E
3,790,430	2/1974	Mochel	65/30 E
3,907,577	9/1975	Kiefer	65/30 E

Primary Examiner—Ellis Robinson

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[57] **ABSTRACT**

An alkali-alumina-silica-zirconia glass capable of being chemically strengthened by exchanging sodium ions in the glass with potassium ions from an external source below the strain point of the glass has its ion exchange rate increased by incorporating 2 to 20 percent P₂O₅ into the initial glass composition.

16 Claims, 3 Drawing Figures

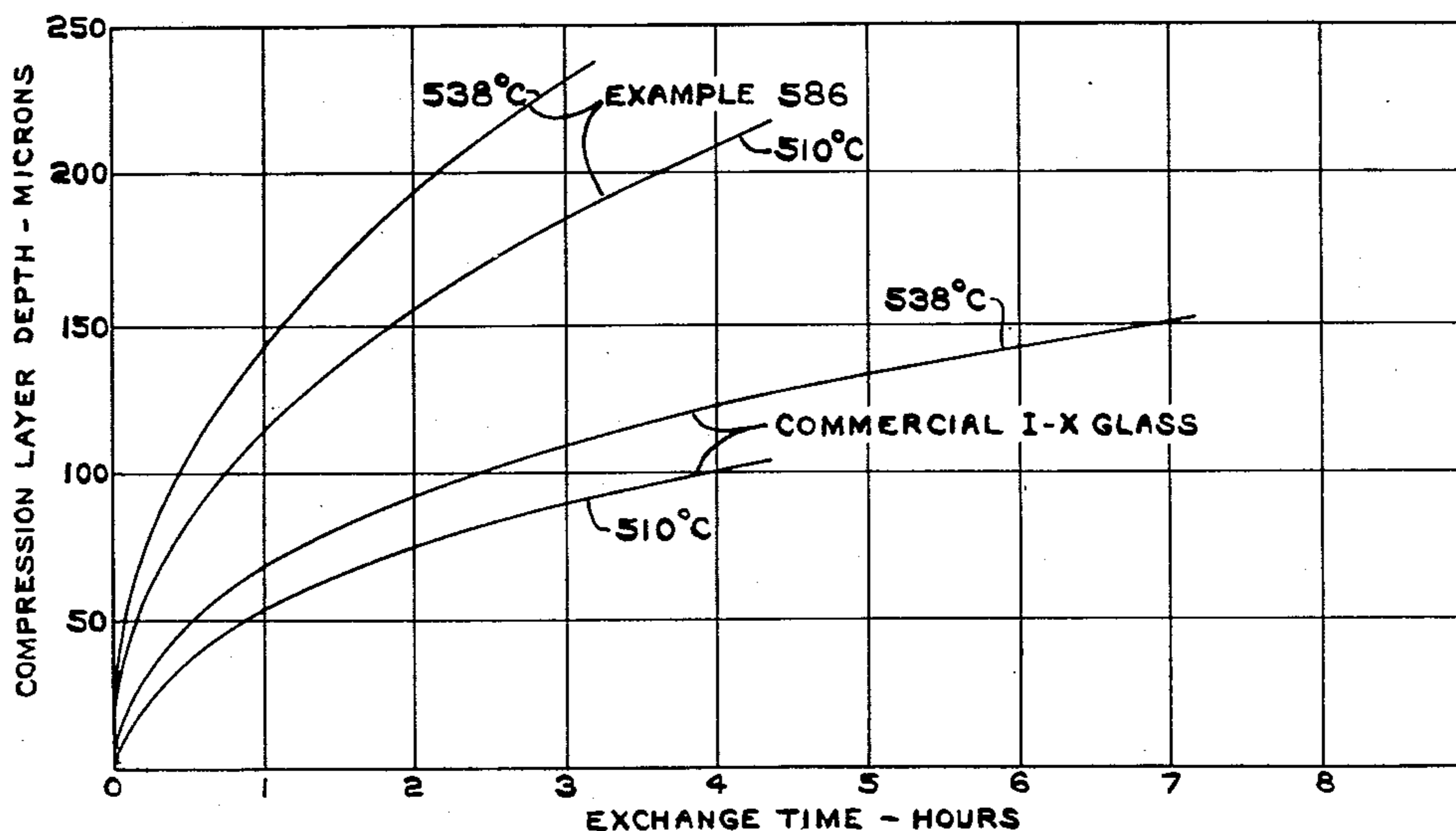


FIG. 1

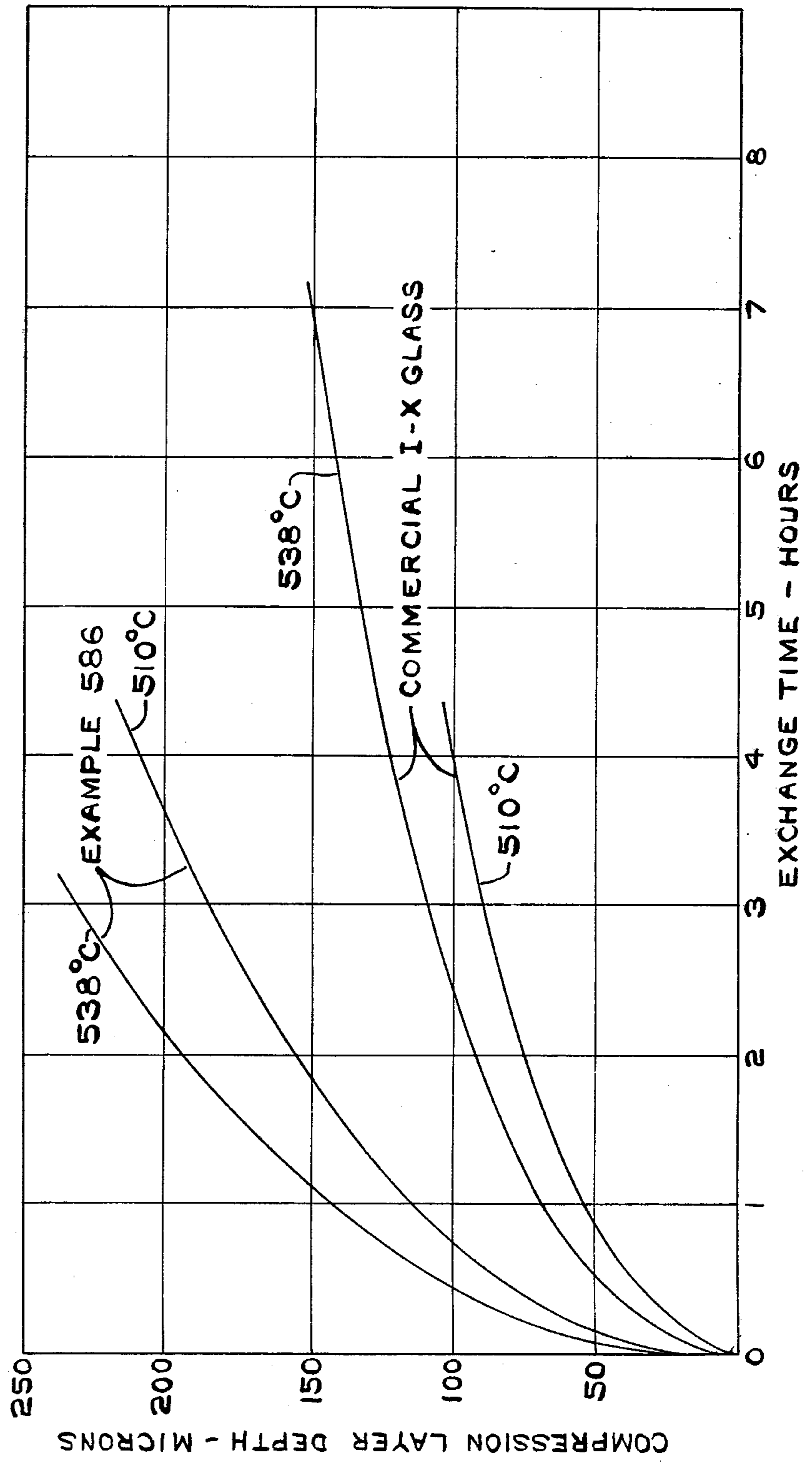


Fig. 2

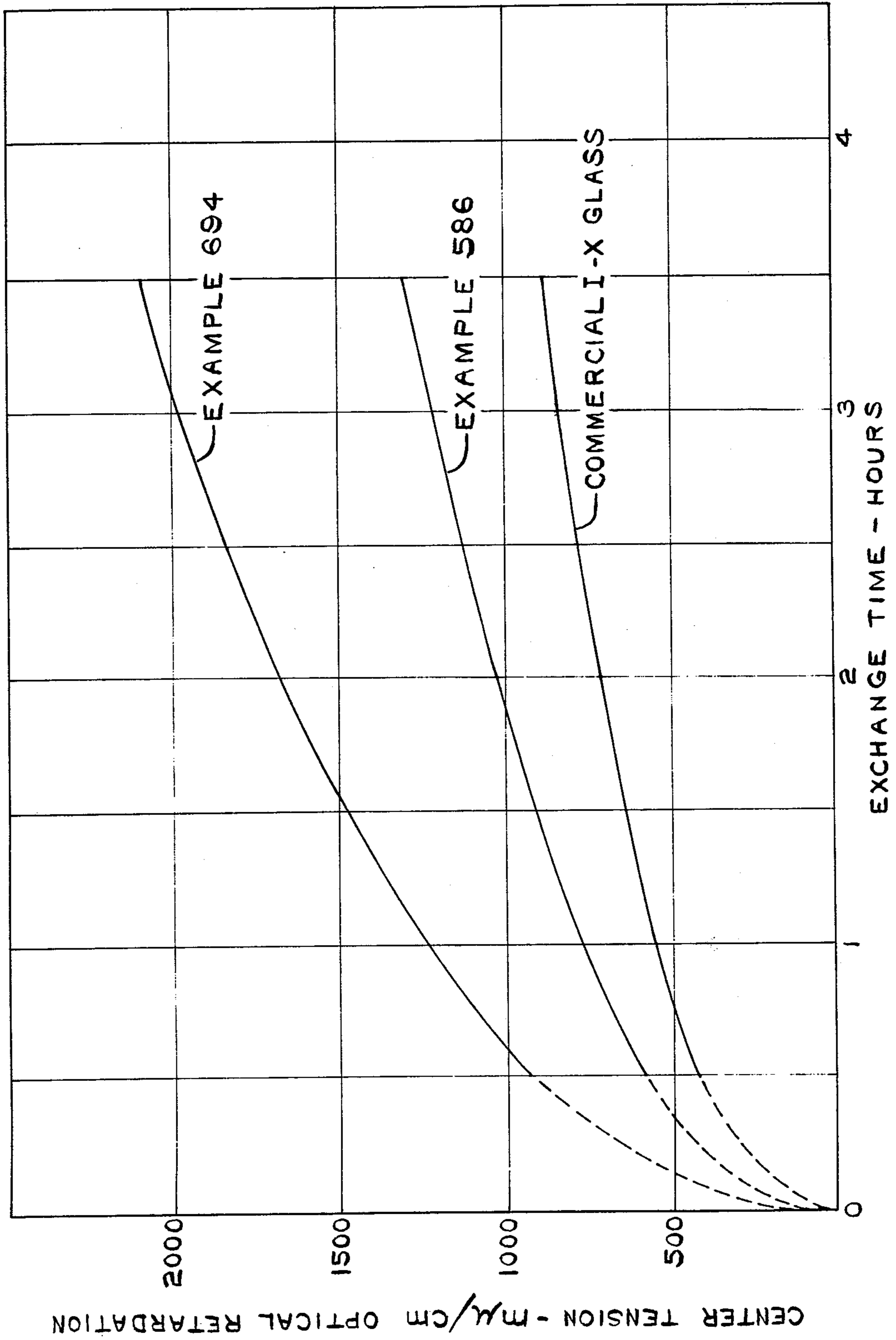
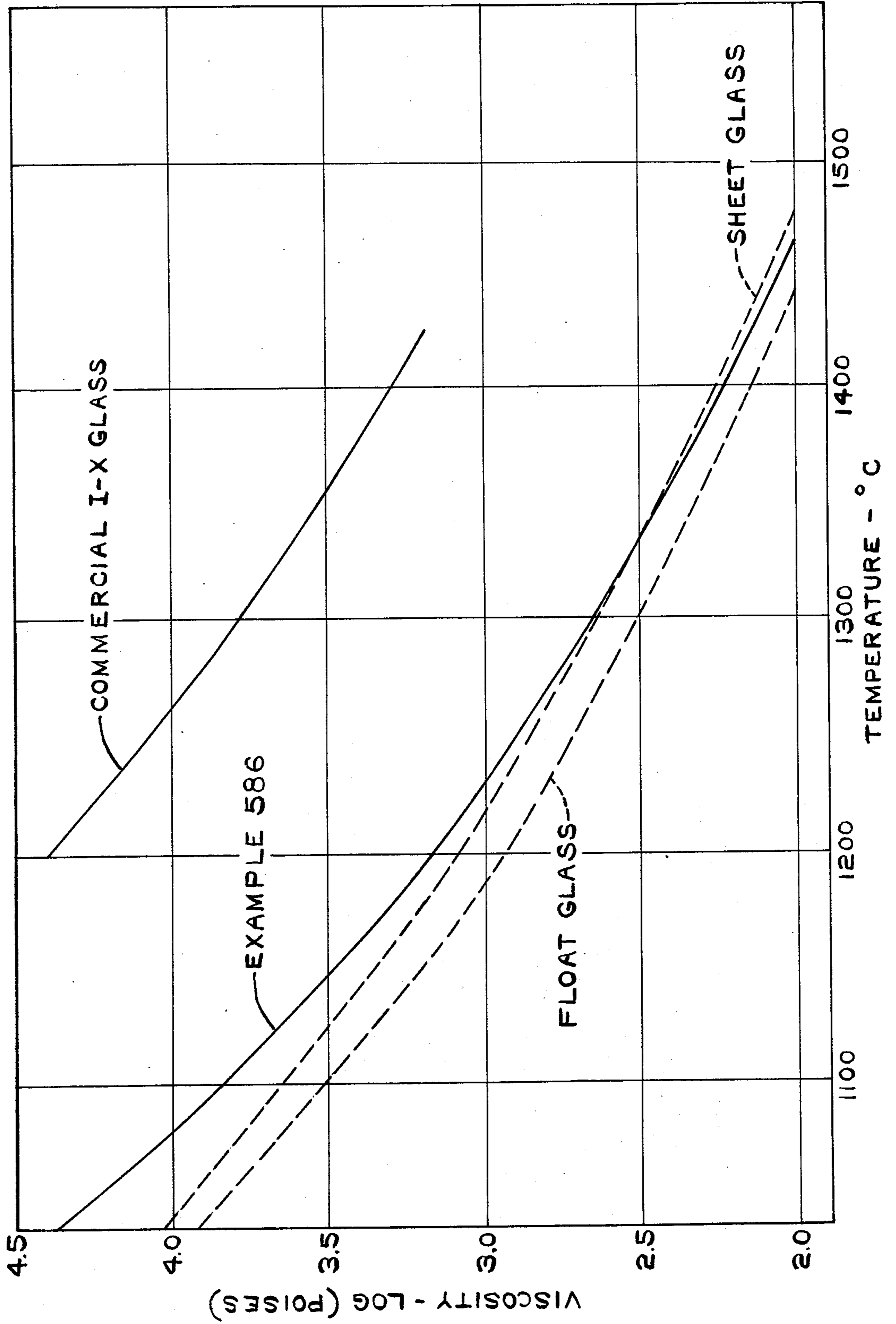


FIG. 3



ION EXCHANGE STRENGTHENED GLASS CONTAINING P₂O₅

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of application Ser. No. 605,108, filed Aug. 15, 1975 now U.S. Pat. No. 4,015,045, which was a continuation-in-part of application Ser. No. 432,006, filed Jan. 9, 1974, now abandoned.

This application is also related in subject matter to applicant's copending application Ser. No. 706,661, filed on even date herewith, entitled CHEMICALLY STRENGTHENED OPAL GLASS.

BACKGROUND OF THE INVENTION

This invention relates to glass compositions and articles made therefrom which are essentially transparent to visible light and are capable of being ion exchange strengthened at an exceptionally high rate of speed. Moreover, the novel glasses of the present invention are rendered suitable for large scale production and subsequent use in automotive, aircraft, architectural, tableware and other applications by virtue of their low melting temperatures and high degree of resistance to chemical attack.

Ion exchange strengthening (or "chemical tempering") of glass involves an exchange of ions near the surface of the glass article with ions from an external source, typically a molten inorganic salt bath, the object being the generation of a zone near the surface of the glass which is in a state of compression relative to the interior portions of the glass. There are two types of ion exchange strengthening which differ substantially in theory and operation. The first type of ion exchange treatment is carried out above the strain point of the glass and has as its object the alteration of the glass composition at the surface so as to lower the thermal coefficient of expansion in the surface layer. As the glass is cooled, a compressive stress develops at the surface due to the expansion differential. This approach was taught by Hood and Stookey in U.S. Pat. No. 2,779,136. The second type of ion exchange strengthening is characterized by treatment below the strain point of the glass, wherein surface compression is generated by substituting large ions from an external source (e.g., a molten salt bath) for smaller ions in the glass. Typically, the substitution is of sodium or potassium for lithium in the glass, or of potassium for sodium in the glass. The below-the-strain-point technique was first taught by Weber in U.S. Pat. No. 3,218,220.

Of the two types of ion exchange strengthening, the second (below the strain point) type is preferred for large-scale commercial use. This is because maintaining the glass below its strain temperature avoids causing undesirable distortion defects in the glass. Furthermore, since it is costly to include lithium in a glass as a batch ingredient, and because greater strengthening can generally be achieved, it is desirable that sodium, rather than lithium, be the ion in the glass which is replaced. In that case, the larger ion which enters the glass is most advantageously potassium. Hence, this invention is directed specifically to the improvement of ion exchange strengthening processes which involve replacing sodium with potassium below the strain point of the glass.

Conventional soda-lime-silica flat glass compositions can be strengthened by ion exchange, but the great

length of time required to produce a significant compression layer depth is incompatible with many high volume commercial operations. For this reason, special glass compositions have been developed which have greatly enhanced ion exchange properties, chief among which are the Al₂O₃ and/or ZrO₂ containing glasses disclosed by Mochel in U.S. Pat. Nos. 3,485,702; 3,752,729; and 3,790,430. Variations of these alumina or zirconia containing glasses may be seen in many U.S. patents including the following (some of which contain lithium):

U.S. Pat. No. 3,357,876 — Rinehart
U.S. Pat. No. 3,433,611 — Saunders et al.
U.S. Pat. No. 3,481,726 — Fischer et al.
U.S. Pat. No. 3,485,647 — Harrington
U.S. Pat. No. 3,498,773 — Grubb et al.
U.S. Pat. No. 3,772,135 — Hara et al.
U.S. Pat. No. 3,778,335 — Boyd
U.S. Pat. No. 3,844,754 — Grubb et al.

While these specially adapted ion exchange glass compositions of the prior art greatly reduce the amount of time required for ion exchange treatment compared to conventional soda-lime-silica glass, the commercial use of lithium-free ion exchange glasses remains limited to low volume specialty items because treatment times are still impractically long for many applications. Moreover, many of the prior art compositions have melting temperatures considerably higher than soda-lime-silica glass and thus are not readily adapted for use in existing melting and forming facilities. Thus, it would be highly desirable to have glass compositions available which could be more rapidly strengthened by exchange treatment with potassium and at the same time be possessed of melting temperatures more in line with ordinary soda-lime-silica glass. Other factors such as transparency, chemical durability, and the cost of raw materials also must be taken into consideration.

Substantial progress toward the above-noted goals was attained by the glass compositions disclosed in parent application Serial No. 605,108, the disclosure of which is hereby incorporated by reference. The present invention represents an even greater improvement over those glasses, particularly in regard to the speed with which a deep compression layer can be created in the glasses.

SUMMARY OF THE INVENTION

It has now been found that an alkali-alumina-zirconia-silica ion exchange glass of the type disclosed in parent application Ser. No. 605,108 can be adapted to include P₂O₅, the result being a significantly enhanced propensity for exchange with potassium ions. At least ninety percent by weight of the glass consists of SiO₂, Na₂O, K₂O, Al₂O₃, ZrO₂, P₂O₅, ZnO, MgO and TiO₂, and the glass is essentially lithium-free. By carefully selecting the amounts of these constituents, it has been found possible to obtain the ion exchange advantages and at the same time produce a glass that is very transparent, low temperature melting, and resistant to chemical erosion.

THE DRAWINGS

FIG. 1 is a plot of compression layer depth versus ion exchange treatment time for a preferred example of the present invention and for a commercially available ion exchange glass at two different temperatures;

FIG. 2 is a plot of center tension versus exchange time for two preferred examples of the present invention and a commercially available ion exchange glass; and

FIG. 3 is a plot of viscosity versus temperature for a preferred example of the present invention, a commercially available ion exchange glass, a typical float glass composition, and a typical sheet glass composition.

DETAILED DESCRIPTION

In its broadest aspects, the novel glass composition of the present invention includes the following:

Component	Percent by Weight, Oxide basis
SiO ₂	34 - 61
Na ₂ O	12 - 20
K ₂ O	2 - 9
(Na ₂ O + K ₂ O)	17 - 23
Al ₂ O ₃	2 - 15
ZrO ₂	0 - 10
(Al ₂ O ₃ + ZrO ₂)	9 - 23
P ₂ O ₅	2 - 20
ZnO	0 - 8
MgO	0 - 6
TiO ₂	0 - 5
(ZnO + MgO + TiO ₂)	2 - 9

The glass includes no more than trace amounts of Li₂O, i.e., no more than about 0.1 percent by weight. The composition may also include small amounts (no more than about 10 percent) of other conventional fluxing ingredients such as BaO, PbO, and B₂O₃.

When about 10 percent or more P₂O₅ is included in the glass, it is necessary to include at least 2 percent ZnO in the glass. Moreover, it is preferred in that case that the (ZnO + MgO + TiO₂) component consist almost entirely of ZnO. Thus, for high phosphate concentrations (10 to 20 percent) the preferred composition is as follows:

Component	Percent by Weight, Oxide Basis
SiO ₂	34 - 52
Na ₂ O	12 - 20
K ₂ O	2 - 9
(Na ₂ O + K ₂ O)	20 - 23
Al ₂ O ₃	8 - 15
ZrO ₂	0 - 9
(Al ₂ O ₃ + ZrO ₂)	10 - 23
P ₂ O ₅	10 - 20
ZnO	2 - 8

At lower P₂O₅ levels (2 to 10 percent) ZnO is not an essential ingredient, but in order to obtain practical melting temperatures, the combined amount of ZnO + MgO + TiO₂ should fall within the range of about 2 to 9 percent. In that case, the preferred composition may be stated as:

Component	Percent by Weight, Oxide Basis
SiO ₂	44 - 61
Na ₂ O	12 - 18
K ₂ O	3 - 9
(Na ₂ O + K ₂ O)	17 - 23
Al ₂ O ₃	2 - 15
ZrO ₂	2 - 10
(Al ₂ O ₃ + ZrO ₂)	9 - 20
P ₂ O ₅	2 - 10
ZnO	0 - 5
MgO	0 - 6
TiO ₂	0 - 5
(ZnO + MgO + TiO ₂)	2 - 9

SiO₂ is the primary glass former and is the largest single component of these glasses. Minimizing the SiO₂ content is desirable so as to lower the melting temperature, but too little SiO₂ can adversely affect durability of the glass. Na₂O is present as a fluxing agent and provides the sites for subsequent ion exchange. Although an excess of Na₂O can reduce the resistance of the glass to chemical attack, at least the minimum amount prescribed should be present in the glass to maintain the melting temperature of the glass at a practical level and to provide the glass with an appreciable ion exchange propensity. K₂O is also desirably present in the glass as a fluxing agent. At higher concentrations, K₂O can lower the strength obtained by ion exchange with potassium, but it has been found that in small amounts K₂O actually tends to improve exchange of sodium by potassium.

The ingredients primarily responsible for practical below-the-strain-point ion exchange strengthening are Al₂O₃ and ZrO₂. The inclusion of excess Al₂O₃ in this type of glass, however, raises its melting temperature substantially and lowers its chemical durability. ZrO₂ does not have these drawbacks, but it has been found that the inclusion of more than a few percent of ZrO₂ in these glasses leads to devitrification which can adversely affect forming operations. However, Al₂O₃ and a limited amount of ZrO₂ tend to make a glass clearer. The aforementioned application Ser. No. 605,108 discloses glass compositions which successfully include both Al₂O₃ and ZrO₂ in such a way as to avoid the drawbacks of both. Although such glasses are excellent ion exchange glasses and represent major improvements, upper limits on their Al₂O₃ and ZrO₂ contents acts as restraints on the ion exchange rates obtainable. The inclusion of P₂O₅ in the glasses here has been found to extend the ion exchange properties of that type of glass beyond previous limits. In particular, the P₂O₅ increases the speed with which a given depth of compression layer can be attained. The P₂O₅ also advantageously raises the strain point and has a beneficial effect on the melting temperature, but an excess may adversely affect chemical durability and homogeneity. However, a high degree of chemical durability can be maintained at the upper end of the P₂O₅ range (i.e., about 15 to 20 percent) if the glass includes no more than about 13 percent Al₂O₃. Furthermore, larger amounts of P₂O₅ than necessary are undesirable from a batch cost standpoint.

One or more of ZnO, MgO, and TiO₂ are present in the glass to aid melting. However, at a P₂O₅ content of about 10 percent or more, the presence of ZnO is essential in order to avoid hazinesses caused by light scattering in the glass. Moreover, at the 10 percent-plus level of P₂O₅, only small amounts of MgO or TiO₂ (preferably none) should be present if the glass is to be clear.

As discussed above, the glasses of the present invention are intended to be lithium-free. However, trace amounts of Li₂O (up to about 0.1 percent by weight) may be tolerated.

Minor amounts of colorants may be added to the compositions in order to produce tinted glass. Many such colorants are known to those of skill in the art and include, for example: CuO, CoO, Cr₂O₃, Fe₂O₃, and MnO.

A major object of the present invention is the production of ion exchange glasses which have melting temperatures similar to that of conventional soda-lime-silica glass. Melting temperature, for the purposes of this

application, is taken as the temperature at which the glass has a viscosity of 100 poises. Since commercial flat glass made by the float process or the sheet updraw process usually exhibit a viscosity of 100 poises at a temperature below about 2800° F. (1538° C.), that temperature is considered herein as being the upper limit for a desirable melting temperature.

The accompanying examples illustrate the effect each of the constituents has on the properties of the glass, and include examples within as well as outside the scope of the present invention. The example glasses were melted from laboratory batch materials including: "Supersil" sand, zircon sand (ZrSiO₄), aluminum metaphosphate, reagent grade ZnO, MgO, Na₂CO₃, K₂CO₃, and Al(OH)₃, and commercial grade TiO₂. The following batch composition, for Example 586, is typical:

Ingredient	Weight (grams)
"Supersil" sand	317.1
Sodium carbonate (anhydrous)	230.9
Aluminum hydrate [Al(OH) ₃]	73.6
Potassium carbonate	33.1
Zircon sand (ZrSiO ₄)	50.8
Aluminum metaphosphate	143.8
Zinc oxide	37.5

The batch ingredients were added incrementally over a period of approximately 3 hours to a 4 inch (10 centimeter) diameter platinum crucible held at about 1450° C. (higher where required). Each melt was stirred during the batch additions and for an additional period of about 15 hours during which the melt was maintained at 1450° C. Thereafter, each melt was held at 1450° C. for about one more hour in a quiescent state, after which a number of rods were drawn from the melt and the remainder of the melt was cast onto a plate.

The depth of the compression layer and the strength obtained after two different ion exchange treatments in molten KNO₃ are reported for many of the examples. Compression layer depth was measured optically on a ground cross-sectional slice sawed from a plate of the ion-exchange glass. Each slice was placed between cross-polaroids under a microscope, where the compression zone could be observed. Strength is reported as modulus of rupture (M.O.R.) obtained by the abraded rod technique. Rods nominally 3 millimeters in diameter drawn from the glass melt were cut into approximately 2.5 inch (6.5 centimeter) lengths and heated at about 650° C. for half an hour, then cooled to room temperature overnight to anneal the rods. After ion exchange treatment, the rods are subjected to tumble

abrasion by being placed in a 16 oz. jar containing 240 grit silicon carbide. The jar is rotated horizontally about its main axis at a speed of about 167 revolutions per minute for 30 minutes. Each abraded rod is then placed singly on a 1.5 inch (3.8 centimeter) support span and stressed to fracture with a $\frac{3}{4}$ inch (1.9 centimeter) wide load member. The load at fracture is recorded, and M.O.R. is calculated by the following formula:

$$\text{M.O.R.} = 8WL/\pi ab^2$$

where W is the load at fracture, L is the difference between the load and support spans, a is the larger diameter of the rod, and b is the smaller diameter of the rod (assuming that the rod is not perfectly circular in cross-section). Each reported M.O.R. value represents the average of at least ten rods.

The annealing points given in the examples were determined by a differential thermal analysis technique. Melting temperature, defined for the purposes of this application as the temperature at which the viscosity of the glass is 100 poises, and forming temperature, defined as the temperature at which the viscosity of the glass is 10,000 poises, were both determined by a standard rotating spindle viscometer technique. Where any of the measurements were duplicated, the values shown in the tables represent averages.

The examples use terms such as "clear," "hazy," and "cloudy" to describe the appearance of the glasses. More precisely, they represent the degree of light scattering observed in each glass by the unaided eye, that is, the sharpness with which an image may be perceived through the glass. Because such a quality is difficult to measure quantitatively, the somewhat subjective terms "clear," "hazy," and "cloudy" are necessarily relied on. "Clear" is intended to mean that the glass appears to be fully transparent (although it may be colored). "Hazy" means that some bluish or whitish iridescence or interference with visibility is detected, particularly at oblique angles, but that images are still at least fairly recognizable through the glass. Glasses which are "cloudy" are difficult to see through and possess a definite whitish cast from all angles. The reported appearances are based on observations of rods and/or plates of each glass with thicknesses of about $\frac{1}{8}$ inch (3 millimeters) to about $\frac{1}{4}$ inch (6 millimeters). It should be noted that the degree of light scattering is independent of light transmittance. Thus, a colored (or "tinted") piece of glass which absorbs a substantial portion of the light striking it may be substantially free from light scattering and would thus be considered "clear".

TABLE I

EXAMPLE NO.:	411	492	493	515	514	501	516	523	534	545
COMPOSITION (% by weight):										
SiO ₂	54.5	52.5	49.5	47.5	46.5	44.5	52.5	39.5	36.5	34.5
Na ₂ O	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0
Al ₂ O ₃	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
MgO	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
K ₂ O	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
ZrO ₂	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5
P ₂ O ₅	—	2.0	5.0	7.0	8.0	10.0	12.0	15.0	18.0	20.0
TiO ₂	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
APPEARANCE:	Clear	Clear	Clear	Clear	Clear	Clear-slight haze	Hazy	Cloudy	Very Cloudy	Almost Opaque
COMPRESSION LAYER DEPTH (microns)										
after 1 hr. at 1000° F (538° C):	54	57	60	70	65	75	85	100	115	130
M.O.R. (Kg/cm ²)										
after 1 hr. at 1000° F (538° C):	4700	4100	3800	5000	5100	5200	5400	5700	5100	—
after 4 hrs. at 900° F (482° C):	5600	5300	5400	5300	5600	6000	6600	6600	6100	—
ANNEALING POINT (° C):	573	566	550	558	562	582	604	621	621	648
MELTING TEMPERATURE (° C):	1416	1417	1398	1390	1379	1372	—	1342	1312	1298
FORMING TEMPERATURE (° C):		1042	1028	1019	1016	1016	—	1001	991	989

Table I shows the effect of progressively substituting P₂O₅ for SiO₂ in a glass of the type disclosed in the parent application, beginning with Example 411, which was a preferred example therein. At 10 percent P₂O₅, a slight haze begins to appear in the glass, which increases to an almost opaque white appearance at 20 percent P₂O₅. However, in Examples 492, 493, 515, and 514 (and marginally in 501) sufficient P₂O₅ was included to signif-

Variations of the same system, with P₂O₅ limited to 10 percent or less, are shown in Table II. As noted, Table II includes glasses which were clear as well as others which were not for the sake of comparison. Example 551 is of particular interest in that, despite the fact that it is a clear glass, it is not a preferred embodiment because of an excessively high melting temperature, due to the absence of MgO and TiO₂.

TABLE II

EXAMPLE NO.:	526	533	544	550	551	554	555	558	560	565	566	
Composition (% by weight):												
SiO ₂	46.0	48.0	48.0	44.0	52.5	50.0	52.5	54.5	49.5	54.5	50.5	
Na ₂ O	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0	
Al ₂ O ₃	12.0	12.0	12.0	10.0	12.0	10.0	10.0	8.0	10.0	4.5	14.0	
MgO	4.5	4.5	2.5	5.5	—	4.5	5.0	4.5	5.0	5.5	4.5	
K ₂ O	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	
ZrO ₂	4.5	4.5	4.5	4.5	4.5	4.5	4.5	2.0	4.0	4.5	10.0	
P ₂ O ₅	10.0	10.0	10.0	10.0	10.0	10.0	7.0	10.0	10.0	10.0	1.0	
TiO ₂	2.0	—	2.0	5.0	—	—	—	—	—	—	—	
Appearance:	Clear-Smoky	Clear	Clear	Hazy	Clear	Clear Slight Haze	Clear	Clear Slight Haze	Clear	Clear	Hazy	
Compression Layer Depth (microns)												
after 1 hr. at 1000° F (538° C):		90	95				90	90	90			
M.O.R. (kg/cm ²)												
after 1 hr. at 1000° F (538° C):	5800	5800	5600	—	3700	4300	4400	2400	4300	2500		
after 4 hrs. at 900° F (482° C):	6000	5800	5600	4900	4700	5500	5200	3900	5800	3800	5400	
Annealing Point (° C):		617	625			598	571		589	566		
Melting Temperature (° C):		1474			1543	1468	1471	1487		1422		
Forming Temperature (° C):		1091			1119	1081	1079	1073		1029		
EXAMPLE NO.:	666	711	721	723	724	745	753	754	792	795	813	814
Composition (% by weight):												
SiO ₂	59.0	44.5	47.5	51.5	50.5	47.5	47.5	45.5	44.5	54.5	56.0	61.0
Na ₂ O	18.0	18.0	12.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0	16.0	17.0
Al ₂ O ₃	10.0	15.0	12.0	10.0	10.0	10.0	12.0	14.0	14.0	10.0	2.0	4.5
MgO	—	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
K ₂ O	3.0	3.0	9.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	—
ZrO ₂	—	4.5	4.5	4.5	4.5	4.5	4.5	4.5	5.5	4.5	10.0	4.5
P ₂ O ₅	10.0	10.0	10.0	8.0	9.0	10.0	10.0	10.0	9.0	5.0	8.0	8.0
TiO ₂						2.0			0.5			
Appearance:	Hazy	Clear Smoky	Clear Smoky	Clear Smoky	Clear	Clear Slight Haze	Clear	Clear Slight Haze	Clear	Clear	Clear	Clear
Compression Layer Depth (microns)												
after 1 hr. at 1000° F (538° C):	120											
M.O.R. (kg/cm ²)												
after 1 hr. at 1000° F (538° C):		6900		4500	4600		6300				3300	—
after 4 hrs. at 900° F (482° C):		8200		6000	6000		6500				4600	3500
Annealing Point (° C):	541											
Melting Temperature (° C):	1574				1474						1462	1537
Forming Temperature (° C):	1024				1085						1098	1114

icantly increase the compression layer depth attained after a one hour exchange treatment, and yet those glasses were found to be clear. Additionally, those examples exhibit very favorable melting temperatures, due in large measure to the presence of MgO and TiO₂.

Table III sets forth numerous attempts to produce a clear ion exchange glass containing more than 10 percent P₂O₅. ZnO was not present, and apparently as a result, none of the attempts successfully produced a clear glass.

TABLE III

EXAMPLE NO.:	527	536	557	608	612	649	657	662	671
COMPOSITION (% by weight):									
SiO ₂	44.5	41.5	46.5	50.0	44.5	49.5	44.5	54.0	48.0
Na ₂ O	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0
Al ₂ O ₃	10.0	10.0	10.0	4.5	10.0	10.0	15.0	10.0	10.0
MgO		5.0		5.0	5.0				
K ₂ O	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
ZrO ₂	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	6.0
P ₂ O ₅	15.0	18.0	18.0	15.0	15.0	15.0	15.0	15.0	15.0
TiO ₂	5.0								
APPEARANCE:	Cloudy	Cloudy	Hazy	Cloudy	Cloudy	Hazy	Slight haze	Hazy	Cloudy
COMPRESSION LAYER DEPTH (microns)									
after 1 hr. at 1000° F (538° C)	115	135	130		125	130	170	125	
M.O.R. (kg/cm ²)									
after 1 hr. at 1000° F (538° C):	3900	5300		4400	5500				
after 4 hrs. at 900° F (482° C):		6100		5300	6100		5300		
ANNEALING POINT (° C):		688	670		642			614	
MELTING TEMPERATURE (° C):		1411	1519			1536		1568	
FORMING TEMPERATURE (° C):		1069	1123			1121		1125	
EXAMPLE NO.:	673	674	675	676	677	687	722	755	
COMPOSITION (% by weight):									
SiO ₂	47.5	46.0	49.0	42.5	40.5	47.0	42.5	39.5	
Na ₂ O	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0	
Al ₂ O ₃	12.0	10.0	15.0	10.0	10.0	10.0	10.0	15.0	

TABLE IV-continued

M.O.R. (kg/cm ²)											
after 1 hr. at 1000° F (538° C):	4000					6000		—	5800		5200
after 4 hrs. at 900° F (482° C):	4300		6000			5600		5400	6400		—
EXAMPLE NO.:	756	757	761	781	783	793	796	803	812	815	819
Composition (% by weight):											
SiO ₂	44.5	36.5	34.5	37.1	38.5	44.5	54.5	40.5	45.5	59.0	49.5
Na ₂ O	18.0	18.0	18.0	17.4	18.0	18.0	18.0	18.0	20.0	16.0	13.0
Al ₂ O ₃	12.0	18.0	15.0	17.0	14.0	4.5	10.0	10.0	10.0	4.5	10.0
MgO	2.0	—	—	1.9	2.0	—	—	—	—	—	—
K ₂ O	3.0	3.0	3.0	2.9	3.0	3.0	3.0	3.0	—	—	3.0
ZrO ₂	4.5	4.5	4.5	4.3	4.5	10.0	4.5	8.5	4.5	4.5	4.5
P ₂ O ₅	12.0	15.0	20.0	14.5	15.0	15.0	5.0	15.0	15.0	11.0	15.0
ZnO	4.0	5.0	5.0	4.8	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Appearance:	Clear	Clear	Clear	Clear	Hazy	Hazy	Clear	Clear	Clear	Slight Haze	Hazy
M.O.R. (kg/cm ²)											
after 1 hr. at 1000° F (538° C):	5500	5500	6500	6800	5900	—	3000	6000	—	—	—
after 4 hrs. at 900° F (482° C):	6300	6800	5700	7000	—	—	4500	6600	5100	2300	—

*White deposits on surface

Table V shows examples of clear, colored glasses within the scope of the present invention.

TABLE V

Example No.:	772	773	774	776	777	787
Composition (% by weight):						
SiO ₂	44.2	44.45	44.2	44.0	44.0	43.5
Na ₂ O	18.0	18.0	18.0	18.0	18.0	18.0
Al ₂ O ₃	10.0	10.0	10.0	10.0	10.0	10.0
MnO ₂	—	—	—	0.5	—	—
K ₂ O	3.0	3.0	3.0	3.0	3.0	3.0
ZrO ₂	4.5	4.5	4.5	4.5	4.5	4.5
P ₂ O ₅	15.0	15.0	15.0	15.0	15.0	15.0
ZnO	5.0	5.0	5.0	5.0	5.0	5.0
CuO	0.3	—	—	—	—	—
CoO	—	0.05	—	—	—	—
Cr ₂ O ₃	—	—	0.3	—	—	—
Fe ₂ O ₃	—	—	—	—	0.5	1.0
Appearance:	Clear Blue	Clear Blue	Clear Green	Clear Purple	Clear Green	Clear Green
M.O.R. (kg/cm ²)						
after 1 hr. at 1000° F (538° C):	5100	4600	4700	—	—	—
after 4 hrs. at 900° F (482° C):	6300	6300	6300	—	—	—

Which of these examples may be considered the most preferred depends upon the particular application for which the glass is intended and the importance placed upon each of the various parameters. One very clear composition which combines a number of desirable properties and appears to be suitable for conventional flat glass applications is Example No. 586. The relative merits of such a composition may be seen by comparing it with a standard, commercially available ion exchange glass sold by Corning Glass Works under the name "Chemcor."

COMPOSITION	EXAMPLE 586	COMMERCIAL ION-EXCHANGE GLASS
SiO ₂	44.5	61.91
Na ₂ O	18.0	12.58
K ₂ O	3.0	3.45
Al ₂ O ₃	10.0	17.43
ZrO ₂	4.5	0.02
P ₂ O ₅	15.0	—
ZnO	5.0	—
CaO	—	0.15
MgO	—	3.46
TiO ₂	—	0.63
Melting temp., ° C.:	1466	1750 (estimated)
Annealing point, ° C.:	674	627
M.O.R. (kg/cm ²)		
(KNO ₃ , 4 hrs. 482° C.):	4800	4300
(KNO ₃ , 4 hrs. 482° C.):	5600	6600

The melting temperature of the commercial ion exchange glass could not be measured directly, but was estimated by extrapolating obtainable viscosity data.

Additional differences between Example 586 and the commercial ion exchange glass are illustrated in the drawings. In FIG. 1, the compression layer depth attained after treatment in molten KNO₃ at two temperatures is plotted against time for both glasses. It is readily apparent that the 586 glass develops a compression layer at a much faster rate than the commercial glass.

FIG. 2 compares the center tension developed in the glasses in terms of optical retardation as measured by the quartz wedge technique. All the glasses were tested on 0.084 inch (6 millimeter) thick samples exchanged for one hour at 1000° F. (538° C.) in molten KNO₃. Center tension is a measure of the stresses created in the interior of the glass in counteraction to the compression stresses in the surface portions, and is directly related to the ability of the treated glass to fragment into small particles upon fracture. The plots in the figure show that the Example 586 glass also has a significantly more rapid buildup of center tension than the commercial ion exchange glass. FIG. 2 also includes a plot for the glass of Example 694, another embodiment, and it is shown to be even faster in developing center tension.

FIG. 3, shows temperature-viscosity curves for Example 586 and the commercial ion exchange glass as well as for ordinary float glass and sheet glass. The float glass and sheet glass have the following compositions (percent by weight, oxide basis):

	Float Glass	Sheet Glass
SiO ₂	73.2%	73.0%
Na ₂ O	13.7	13.3
K ₂ O	0.03	0.2
CaO	8.9	8.2
MgO	3.9	3.7
Al ₂ O ₃	0.1	1.2
SO ₃	0.2	0.2
Fe ₂ O ₃	0.1	0.1

The plot for glass 586 advantageously lies very close to the plots for sheet and float glass, but in contrast it is readily apparent from the figure that the commercial ion exchange glass is much more difficult to melt than sheet or float glass.

The advantages of rapid compression layer development are considerable. Strength of a particular treated glass as measured by M.O.R. values is by itself seldom sufficient to indicate that a glass article will actually have significantly improved strength when put into service. This is because a high degree of compression

can sometimes be concentrated in a very thin layer near the surface of the glass, which, when abraded or scratched in use, can lose its strengthening effect. Therefore, the most demanding requirement for many applications is the need to generate a compression layer deep enough to withstand the physical abuses to which the surface of the glass may be subjected. In this light, it is interesting to compare the treatment times required to obtain a given compression layer thickness as follows:

Glass	Compression Layer Thickness	Treatment In KNO_3	Abraded Rod M.O.R.
Example 586	150 microns	1.2 hrs. at 538° C	4800 kg/cm ²
Example 586	150 microns	2 hrs. at 510° C	5500 kg/cm ²
Commercial I-X	150 microns	7.3 hrs. at 538° C	5000 kg/cm ²
Commercial I-X	150 microns	9.6 hrs. at 510° C	5800 kg/cm ²

It can be seen that for a fixed compression layer depth, M.O.R. values for the Example 586 glass were almost the same as for the commercial ion exchange glass, yet the compression layer in 586 was developed in a fraction of the time required by the commercial glass. The minimum compression layer depth required will depend upon the particular end use of the glass, but theoretically the compression layer need extend only beyond the deepest penetration of surface defects in order for the glass to be strengthened. This has been estimated to be about five microns in the case of a glass plate subjected to reasonably careful handling.

It should be apparent that the increase in glass strength attained by ion exchange will vary by degree, ranging from a de minimis effect to a many-fold increase. For many applications, however, it is preferred that the strengthening be at least as great as that achieved by thermal tempering of glass. Thermal usually at least doubles the M.O.R. of float glass, or increases the M.O.R. to a value in the area of about 1700 kg/cm² or more. The degree to which glass strength may be enhanced by ion exchange is illustrated in the following comparison of abraded rod M.O.R. values:

	No Ion Exchange	After Ion Exchange in KNO_3	
		1 hr. 538° C	4 hrs. 493° C
Example 586:	550 kg/cm ²	4800 kg/cm ²	5600 kg/cm ²
Float glass:	460 kg/cm ²	690 kg/cm ²	820 kg/cm ²

The chemical durability of the glasses of Example 586 was compared with that of commercial float glass having the composition set forth above. The tests were run on glass discs about 2.5 inches (6.35 centimeters) in diameter formed by casting the glass onto a plate. Without being ion exchanged, the discs were immersed in boiling 2 percent by weight sulfuric acid for 30 minutes, after which they were removed from the acid and measured for weight loss. Other discs were subjected to boiling 0.1 Normal NaOH for 30 minutes, with the following results:

	Example 586	Float Glass
Weight loss in acid (milligrams/cm ²)	0.003	0.002
Weight loss in alkali (milligrams/cm ²)	0.004	0.043

These results show the novel compositions to have chemical durability comparable to, or even better than,

float glass, rendering them suitable for use in a wide variety of applications.

Radiant energy transmittance of Example 586 may be compared with float glass as follows for $\frac{1}{4}$ inch (6 millimeter) thickness:

	Example 586	Float Glass
Luminous	90.1%	89%
Ultraviolet	67.1%	70%
Infrared	88.9%	68%
Total Solar Energy	88.8%	78%
Dominant wavelength	574 m μ	499 m μ

The details of the process which the ion exchange treatment is carried out are well known in the art and need not be elaborated upon in great length here. In general, it can be said that the type of ion exchange treatment to which this invention pertains is limited to temperatures below the strain point of the glass, but it should be understood that temperatures at, or slightly above, the strain point are permissible as long as the glass does not remain at such a temperature for sufficient length of time to cause appreciable relaxation of the induced compression at the surface of the glass. In other words, the exchange bath temperature may be slightly above the strain point if the treatment time is short. It is preferred that the highest temperature possible be used in order to shorten treatment time; in other cases it is desirable to ion-exchange more slowly to obtain greater strength. Typically, temperatures on the order of 400° to 600° C. are employed. In addition to KNO_3 , other molten salts of potassium may constitute the exchange bath, such as the chloride, fluoride, or phosphate salts. Other methods of contacting the glass with the exchange medium besides immersing in a molten salt bath have been proposed. These include spraying and coating with a carrier, which may be adaptable to the ion exchange treatment of the glass compositions disclosed herein.

Other modifications and variations as are known in the art may be resorted to without departing from the spirit and scope of the invention as defined by the appended claims.

I claim:

1. A glass essentially transparent to visible light and capable of being strengthened by ion exchange with potassium ions, comprising by weight on the oxide basis:

- 34 to 61 percent SiO_2
- 12 to 20 percent Na_2O
- 2 to 9 percent K_2O
- 17 to 23 percent $(\text{Na}_2\text{O} + \text{K}_2\text{O})$
- 2 to 15 percent Al_2O_3
- 0 to 10 percent ZrO_2
- 9 to 23 percent $(\text{Al}_2\text{O}_3 + \text{ZrO}_2)$
- 2 to 20 percent P_2O_5
- 0 to 8 percent ZnO
- 0 to 6 percent MgO
- 0 to 5 percent TiO_2
- 2 to 9 percent $(\text{ZnO} + \text{MgO} + \text{TiO}_2)$
- 0 to 0.1 percent Li_2O

wherein said constituents comprise at least 90 percent by weight of the glass and are proportioned relative to one another so as to provide the glass with a viscosity of 100 poises at a temperature less than 2800° F. (1538° C.)

2. The glass of claim 1 wherein the composition comprises by weight on the oxide basis:

- 44 to 61 percent SiO₂
- 12 to 18 percent Na₂O
- 3 to 9 percent K₂O
- 17 to 23 percent (Na₂O + K₂O)
- 2 to 15 percent Al₂O₃
- 2 to 10 percent ZrO₂
- 9 to 20 percent (Al₂O₃ + ZrO₂)
- 2 to 10 percent P₂O₅
- 0 to 5 percent ZnO
- 0 to 6 percent MgO
- 0 to 5 percent TiO₂
- 2 to 9 percent (ZnO + MgO + TiO₂)

3. The glass of claim 1 wherein the composition consists essentially of by weight on the oxide basis:

- 34 to 52 percent SiO₂
- 12 to 20 percent Na₂O
- 2 to 9 percent K₂O
- 20 to 23 percent (Na₂O + K₂O)
- 8 to 15 percent Al₂O₃
- 0 to 9 percent ZrO₂
- 10 to 23 percent (Al₂O₃ + ZrO₂)
- 10 to 20 percent P₂O₅
- 2 to 8 percent ZnO

4. A chemically strengthened transparent glass article exhibiting a surface compressive stress after being subjected to surface abrasion composed of an interior portion which is in tension and a surface compressive layer, said interior portion comprised of by weight on the oxide basis:

- 34 to 61 percent SiO₂
- 12 to 20 percent Na₂O
- 2 to 9 percent K₂O
- 17 to 23 percent (Na₂O + K₂O)
- 2 to 15 percent Al₂O₃
- 0 to 10 percent ZrO₂
- 9 to 23 percent (Al₂O₃ + ZrO₂)
- 2 to 20 percent P₂O₅
- 0 to 8 percent ZnO
- 0 to 6 percent MgO
- 0 to 5 percent TiO₂
- 2 to 9 percent (ZnO + MgO + TiO₂)
- 0 to 0.1 percent Li₂O

said constituents comprising at least 90 percent by weight of the interior portion and proportioned relative to one another so as to provide a glass having a viscosity of 100 poises at a temperature less than 2800° F. (1538° C.), said surface compressive layer having a higher content of K₂O and a lower content of Na₂O than the interior portion.

5. The glass article of claim 4 wherein said interior portion is comprised of by weight on the oxide basis:

- 44 to 61 percent SiO₂
- 12 to 18 percent Na₂O
- 3 to 9 percent K₂O
- 17 to 23 percent (Na₂O + K₂O)
- 2 to 15 percent Al₂O₃
- 2 to 10 percent ZrO₂
- 9 to 20 percent (Al₂O₃ + ZrO₂)
- 2 to 10 percent P₂O₅
- 0 to 5 percent ZnO
- 0 to 6 percent MgO
- 0 to 5 percent TiO₂
- 2 to 9 percent (ZnO + MgO + TiO₂).

6. The glass article of claim 4 wherein said interior portion consists essentially of by weight on the oxide basis:

- 34 to 52 percent SiO₂
- 12 to 20 percent Na₂O
- 2 to 9 percent K₂O
- 20 to 23 percent (Na₂O + K₂O)
- 8 to 15 percent Al₂O₃
- 0 to 9 percent ZrO₂
- 10 to 23 percent (Al₂O₃ + ZrO₂)
- 10 to 20 percent P₂O₅
- 2 to 8 percent ZnO.

7. The glass article of claim 4 wherein said surface compressive layer is at least 50 microns thick.

8. The glass article of claim 4 wherein the surface compressive layer is at least 100 microns thick.

9. The glass article of claim 4 wherein its strength, as measured by abraded rod modulus of rupture, is at least 1700 kilograms per square centimeter.

10. A method of strengthening a transparent glass article comprising the steps of:

a. contacting a source of potassium ions with the surface of a glass article comprising by weight on the oxide basis:

- 34 to 61 percent SiO₂
- 12 to 20 percent Na₂O
- 2 to 9 percent K₂O
- 17 to 23 percent (Na₂O + K₂O)
- 2 to 15 percent Al₂O₃
- 0 to 10 percent ZrO₂
- 9 to 23 percent (Al₂O₃ + ZrO₂)
- 2 to 20 percent P₂O₅
- 0 to 8 percent ZnO
- 0 to 6 percent MgO
- 0 to 5 percent TiO₂
- 2 to 9 percent (ZnO + MgO + TiO₂)
- 0 to 0.1 percent Li₂O

said constituents comprising at least 90 percent by weight of the glass article and proportioned relative to one another so as to provide a glass having a viscosity of 100 poises at a temperature less than 2800° F. (1538° C.);

b. heating said source of potassium ions while in contact with the glass to a temperature at which potassium ions from said source replace sodium ions in the glass, but essentially below the strain point of the glass, thereby creating a zone of compression at the surface of the glass which extends at least 5 microns into the glass; and

c. removing the glass from contact with the potassium ion source.

11. The method of claim 10 wherein the glass article being strengthened initially comprises by weight on the oxide basis:

- 44 to 61 percent SiO₂
- 12 to 18 percent Na₂O
- 3 to 9 percent K₂O
- 17 to 23 percent (Na₂O + K₂O)
- 2 to 15 percent Al₂O₃
- 2 to 10 percent ZrO₂
- 9 to 20 percent (Al₂O₃ + ZrO₂)
- 2 to 10 percent P₂O₅
- 0 to 5 percent ZnO
- 0 to 6 percent MgO
- 0 to 5 percent TiO₂
- 2 to 9 percent (ZnO + MgO + TiO₂)
- 0 to 0.1 percent Li₂O

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said constituents comprising at least 90 percent by weight of the glass article.

12. The method of claim 10 wherein the glass article being strengthened initially comprises by weight on the oxide basis:

- 34 to 52 percent SiO₂
- 12 to 20 percent Na₂O
- 2 to 9 percent K₂O
- 8 to 15 percent Al₂O₃
- 0 to 9 percent ZrO₂
- 10 to 23 percent (Al₂O₃ + ZrO₂)
- 10 to 20 percent P₂O₅
- 2 to 8 percent ZnO

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0 to 0.1 percent Li₂O
said constituents comprising at least 90 percent by weight of the glass article.

13. The method of claim 10 wherein said contacting and heating step are continued for no more than one hour and thereby produce a compression layer at least 50 microns deep at the surface of the glass.

14. The method of claim 13 wherein the compression layer produced is at least 100 microns deep.

15. The method of claim 13 wherein the abraded rod modulus of rupture for the glass is at least doubled by the ion exchange treatment.

16. The method of claim 10 wherein the source of potassium ions is a molten bath of KNO₃.

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